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Certificate

AMIS0650

Certified Reference Material

Magnesite MOXHQ, South Africa

Certificate of Analysis

AMIS

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Summary Statistics

Recommended Concentrations and Limits (at two Standard Deviations) Certified Concentrations

Analyte	Method	⁵ (μ)	⁷ (2s) ±	Unit
Mg	XRF ¹	51.43	1.1	%
Mg	4A_MICP ²	51.22	1.8	%
MgO	XRF	85.72	1.8	%
LOI	LOI ³	8.65	0.62	%
SG	SG ⁴	3.23	0.90	Dimensionless
Al	4A_MICP	1313	192	ppm
Bi	4A_MICP	0.1	0.05	ppm
Ca	4A_MICP	1.06	0.069	%
Cd	4A_MICP	0.05	0.03	ppm
Ce	4A_MICP	1	0.5	ppm
Cu	4A_MICP	15	5	ppm
La	4A_MICP	0.6	0.3	ppm
Mo	4A_MICP	0.2	0.1	ppm
Na	4A_MICP	1431	151	ppm
Ni	4A_MICP	8	2	ppm
Pb	4A_MICP	14	3	ppm
Rb	4A_MICP	1	0.3	ppm
Sb	4A_MICP	0.8	0.4	ppm
Sr	4A_MICP	192	29	ppm
U	4A_MICP	0.3	0.04	ppm
W	4A_MICP	0.5	0.2	ppm
Zn	4A_MICP	13	4	ppm

Major Oxides Certified Concentrations (at two Standard Deviations)

Analyte	Method	⁵ (μ)	⁷ (2s) ±	Unit
Al ₂ O ₃	XRF	0.24	0.04	%
CaO	XRF	1.52	0.13	%
Fe ₂ O ₃	XRF	0.27	0.05	%
SiO ₂	XRF	3.13	0.26	%

1. Certified Concentrations and Uncertainties

AMIS0650 is a new standard material, developed and certified in November 2019. Table 1 gives the certified concentrations, confidence interval, combined and expanded uncertainty for the certified reference material. Table 2 shows the certified major oxides concentrations, two standard deviations, confidence interval, combined and expanded uncertainty.

Table 1. Certified concentrations, two standard deviations, combined and expanded uncertainty.

Analyte	Method	⁵ (μ)	N	n	k	% RSD	⁶ (u_c)	⁷ (2s) \pm	⁸ (CI) 95%	⁹ (U) \pm	Unit
Mg	XRF ¹	51.43	6	48	2.571	1	0.55	1.1	0.56	1	%
Mg	4A_MICP ²	51.22	2	16	12.706	2	0.88	1.8	5.4	11	%
MgO	XRF	85.72	6	48	2.571	1	0.92	1.8	0.94	2	%
LOI	LOI ³	8.65	6	48	2.571	4	0.31	0.62	0.26	1	%
SG	SG ⁴	3.23	2	16	12.706	14	0.45	0.90	4.0	6	Dimensionless
Al	4A_MICP	1313	3	24	4.303	7	96	192	164	413	ppm
Bi	4A_MICP	0.1	2	16	12.706	31	0.02	0.05	0.2	0.3	ppm
Ca	4A_MICP	1.06	5	37	2.776	3	0.034	0.069	0.030	0.1	%
Cd	4A_MICP	0.05	2	16	12.706	28	0.01	0.03	0.1	0.2	ppm
Ce	4A_MICP	1	2	16	12.706	24	0.3	0.5	2	3	ppm
Cu	4A_MICP	15	5	38	2.776	17	2	5	3	7	ppm
La	4A_MICP	0.6	3	24	4.303	24	0.1	0.3	0.3	1	ppm
Mo	4A_MICP	0.2	3	23	4.303	39	0.07	0.1	0.1	0.3	ppm
Na	4A_MICP	1431	4	32	3.182	5	76	151	105	241	ppm
Ni	4A_MICP	8	4	32	3.182	14	1	2	1	3	ppm
Pb	4A_MICP	14	5	36	2.776	10	1	3	2	4	ppm
Rb	4A_MICP	1	4	30	3.182	11	0.2	0.3	0.2	1	ppm
Sb	4A_MICP	0.8	4	31	3.182	23	0.2	0.4	0.2	1	ppm
Sr	4A_MICP	192	5	40	2.776	7	14	29	17	40	ppm
U	4A_MICP	0.3	3	23	4.303	6	0.02	0.04	0.04	0.09	ppm
W	4A_MICP	0.5	2	16	12.706	18	0.08	0.2	0.6	1	ppm
Zn	4A_MICP	13	4	32	3.182	15	2	4	3	6	ppm

Table 2. Certified major oxides concentrations, two standard deviations, combined and expanded uncertainty.

Analyte	Method	⁵ (μ)	N	n	k	% RSD	⁶ (u_c)	⁷ (2s) \pm	⁸ (CI) 95%	⁹ (U) \pm	Unit
Al ₂ O ₃	XRF	0.24	6	47	2.571	8	0.02	0.04	0.02	0.05	%
CaO	XRF	1.52	7	54	2.447	4	0.065	0.13	0.063	0.2	%
Fe ₂ O ₃	XRF	0.27	7	52	2.447	9	0.02	0.05	0.02	0.06	%
SiO ₂	XRF	3.13	6	48	2.571	4	0.13	0.26	0.13	0.3	%

1. XRF is X-ray Fluorescence
2. 4A_MICP is a Multi-acid digestion with either ICPOES/ICPMS/AAS finish
3. LOI is Loss on Ignition
4. SG is Specific Gravity
5. The certified value μ , is an unweighted grand mean of the means of N accepted sets of data from different laboratories and n number of test sample replicates. The certified value is traceable to SI units and is reported on a dry basis.
6. The combined uncertainty of the certified value is the within-laboratory reproducibility standard deviation derived from the analysis of variance of results from N number of laboratories and n number of sample replicates. (u_c)
7. Two standard deviations (2s)
8. Confidence interval at 95% level of confidence.
9. Expanded uncertainty (U) at a confidence level of 95% is determined by multiplication of the combined uncertainty (u_c) with a coverage factor (k) found from N-1 degrees of freedom (see Appendix 7 for t-distribution table). Example: $U = 2.36 \times 0.23 = 0.5\%$
10. FUS is Fusion digestion with ICPOES/ICPMS/AAS finish
11. Combustion/LECO
12. 4A_AAS is a Multi-acid digestion with AAS finish
13. LOI gravimetric is Loss on Ignition with gravimetric finish
14. LOI TGA is Loss on Ignition with TGA finish
15. LOI XRF is Loss on Ignition with XRF finish
16. Ext is Extraction with HCl
17. Moisture

2. Statistical Comparison of Means

A comparison of means for replicate data for the same element concentration determined by different analytical methods is done equating the variances between the two data sets; if the variances are found to be equal (F-test, p -value >0.05), then an equal variance t-test is applied. Should the variances be statistically significant, i.e. $p<0.05$, then an unequal variance t-test is performed. For either t-test, if the obtained p -value ≥ 0.05 , the null hypothesis that the means (certified values) are equal is accepted (Table 3). This gives the analyst confidence in the certified values reported by different analytical methods on the same analyte.

Table 3. The results of a two-sample equal or unequal variance t-test (two-tailed) data sets in which different analytical methods /instrumentation were used.

Method	Certified value	Method	Certified value	F-Test Outcome	p -value (t-test)	t-test Outcome
Mg XRF	51.43 %	Mg 4A_MICP	51.22 %	Equal Variance ($p=0.312$)	0.657	Accept H_0 ; certified values are equal

3. Intended Use

AMIS0650 is a matrix matched Certified Reference Material, fit for use as a control sample in routine assay laboratory quality control when inserted within runs of test samples and measured in parallel to test samples. This material can also be used for method development, use as independent calibration verification check standard (i.e. if not used as a calibration standard in an instrument calibration), or for validation of accuracy in a method validation exercise (see Appendix 3). The recommend procedure for the use of this CRM as a control standard in laboratory quality control is to develop a Shewhart chart, where a mean value and corresponding 1, 2 and 3 standard deviations are derived from replicate measurements of the CRM (see Appendix 6). This CRM can also be used to assess inter-laboratory or instrument bias and establish within-laboratory precision and within-laboratory reproducibility. The certified concentrations and expanded uncertainty for this material are property values based on an inter-laboratory measurement campaign and reflect consensus results from the laboratories that took part in the exercise.

4. Abbreviations and Symbols

Abbreviations and symbols used in this document are shown in Table 4.

Table 4. Abbreviations, symbols and descriptions.

Abbreviation/Symbol	Description
Alpha (α)	Significance level (denoted by alpha, ' α ') of 0.05 or 5%
ANOVA	Analysis of variance by statistical means
Bq	The becquerel is the SI derived unit of radioactivity.
BIF	Banded iron formation
CRM	Certified reference material
df	Degrees of freedom, typically, $n-1$, or $N-1$
F_{calc}	Calculated F statistic from ANOVA or Fisher's test
F-critical or F_{crit}	F-critical value from F-distribution table
GOI	Gain on ignition
H_0	Null hypothesis
H_1	Alternate hypothesis
g/t	Grams per tonne
k	Coverage factor, e.g. $k=2$ for 95% level of confidence
LOC	Level of confidence or confidence level
LOD	Limit of detection
LOQ	Limit of quantitation
LOI	Loss on ignition
MS	Mean squares (ANOVA)
MSb	Mean squares between(ANOVA)
MSw	Mean squares within (ANOVA)
N	Number of labs
n	Number of replicates
μ	Property or certified value of a CRM
p	' p -value' a measure of the strength of evidence against H_0
P	Total number of data points in ANOVA
ppm	Parts per million. Equivalent to g/t
RSD	Relative standard deviation usually expressed as % at a 68% LOC
Replicates	Replication is the repetition of an experimental condition so that the variability associated with an analysis can be estimated (ASTM E1847)
s	Standard deviation
s_r	Within laboratory repeatability as derived from ANOVA
s_s	Between laboratory standard deviation as derived from ANOVA
SS	Sum of squares in ANOVA
SST	Total variation in ANOVA
SSB	Between group (laboratory) variance
SSW	Within group (laboratory) variance

Abbreviation/Symbol	Description
2s	Two times standard deviation
SI	Standard International system of units
t_{calc}	Calculated t statistic from a one-sample, two-tailed t-test
t-critical or t_{crit}	t-critical value at given alpha and degrees of freedom
Tonne	A metric ton, is a unit of mass equaling 1000 kilograms
=TINV(5%, df)	MS Excel function for t-critical value at LOC 95% and df
U	Expanded uncertainty at a given k
u	Standard uncertainty at k=1
u_c	Combined standard uncertainty at $k=1$
μm	Micron, is an SI derived unit of length equaling 1×10^{-6} of a meter

5. Uncertified Concentration Values

Appendix 1 gives uncertified concentrations for other elements present in the CRM.

6. Units

All results for major oxides are reported as oxides in percentages. All results for major elements analyses reported in percentages or ppm. Results for Au and the platinum group elements are reported in g/t or ppm. Specific gravity (SG) is the ratio of the density of a substance to the density of a reference substance, *i.e.* equivalently; it is the ratio of the mass of a substance to the mass of a reference substance for the same given volume. Since specific gravity is a ratio of densities its units are therefore dimensionless.

7. Analytical and Physical Methods

A complete list of analytical and physical methods as generic method codes with a brief description of the methods is available on the AMIS web site www.amis.co.za

8. Origin of Material

The material is from Syferfontein Carbonates in South Africa.

9. Approximate Mineral and Chemical Composition

Magnesite is a magnesium carbonate mineral with a chemical composition of $MgCO_3$. Iron, manganese, cobalt and nickel may occur as admixtures but only in small amounts.

10. Quantitative Analysis by X-Ray Diffraction

Both natural and synthetic materials have a specific chemistry and atomic arrangement, known as phases. Phases can be identified and quantified using X-ray diffraction (XRD) which produces a plot of the intensity of X-rays scattered at different angles by crystalline phases in a material. Essentially, an X-ray diffraction pattern is the sum of the diffraction patterns produced by each phase. Simply put, an X-ray diffraction pattern is a fingerprint that allows the identification of what is in a target sample material. Knowledge of the mineral phase composition is useful in method development with techniques such as ICP-OES and XRF as potential matrix effects and spectral interferences can be recognised

and accounted for. X-ray diffraction is effective in that it allows the identification of different phases of compounds that are identical in chemistry, but have a distinctly different the atoms, e.g. quartz, cristobalite, and glass are all different phases of SiO₂. Where quantitative XRD results do not correspond to results of other analytical techniques, it should be borne in mind that even though the data are quantitative they are meant to be used for indicative purposes in development of other analytical methods. Mineral names may not reflect the actual compositions of minerals identified, but rather the mineral group.

Quantification is determined from the chosen software package: this uses the full-profile Rietveld method of refining the profile of the calculated XRD pattern against the profile of the measured XRD pattern. The total calculated pattern is the sum of the calculated patterns of the individual phases. Results are given as weight % of the total crystalline phases and amorphous content. The amorphous content quantifies the amorphous material and unknown minerals or known minerals for which there is not a suitable crystal structure.

Corrections are incorporated into the process that allows for a more accurate description of the mineral's contribution to the measured pattern and to allow for variation due to atomic substitution, layer disordering, preferred orientation, and other factors that affect the acquisition of the XRD scan.

The limitations of qualitative XRD analysis are as follows:

- The detection of a phase may be dependent on its crystallinity.
- Where there exist multiple phases, overlap of diffracted reflections can occur, thus rendering some ambiguity into the interpretation.
- Overlapping reflections of a major phase can mask the presence of minor or trace phases.
- Some phases cannot be unambiguously identified as they are present in minor or trace amounts.

The limitations of quantitative XRD analysis by a full-profile Rietveld method are as follows:

- The limitations for qualitative XRD analysis apply.
- The method as described is standardless: it relies solely on the published crystallographic data available for each phase. Some data may not exactly describe the phases present.
- Particle size is important with respect to the absorption of the X-rays by the sample.
- Micronising reduces the particle size to that more suitable for quantitative analysis.

The accuracy of the analysis is dependent on sampling and sample preparation in addition to the calculated profiles being exactly representative of the chemistry of the component phases and their crystallinity. Some preferred orientation effects and reflection overlaps may occur which cannot be adequately resolved.

Table 5. Results of XRD analysis.

Phase	Formula	Composite
Amorphous Content		11
Calcite	CaCO ₃	<1
Dolomite	CaMg(CO ₃) ₂	1
Periclase	MgO	84
Quartz	SiO ₂	3
Total		99

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11. Health and Safety

The material is a very fine powder coloured White (Corstor 8/N). Safety precautions for handling fine particulate matter are recommended, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.

12. Method of Preparation

The particle size distribution for this material was shown to have a nominal top size of 54µm (95% passing 54µm). The procedure of preparation in brief is as follows: the material was crushed, dry-milled and air-classified to <54µm. It was then blended in a bi-conical mixer, systematically divided and sealed into 1kg Laboratory Packs. Explorer Packs are then subdivided from the Laboratory Packs as required. Final packaged units were then selected on a random basis and submitted for analysis to an independent laboratory accredited with the ISO17025 standard of general requirements for the competence of testing and calibration laboratories. The results obtained from this laboratory are then evaluated statistically by AMIS for homogeneity.

13. Particle Size Determination

The sample has been analysed using a Malvern Mastersizer 2000. Particles are passed through a focused laser beam that scatter light at an angle inversely proportional to their size. The intensity of light is measured and converted to a volume in particle size distribution. The results for this standard are presented in Table 6.

Table 6. Particle Size Determination by laser diffraction.

Size (µm)	Vol. Under %
<45 µm	96.9
<63 µm	98
<75 µm	98.3
<90 µm	98.9
<100 µm	99.2
<106 µm	99.3
<150 µm	99.9

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14. Handling

The material is packaged in Laboratory Packs and Explorer Packs that must be shaken or otherwise agitated before use. The analyte concentrations are quoted on a dry basis; therefore, the user needs to determine the moisture content to convert any obtained assay values to an air-dry basis (see Appendix 7 for an example calculation).

15. Storage information

The material should be stored in a cool dry place, in such a way that it does not compromise the integrity of the CRM. The material should be stored in conditions which will ensure it does not absorb moisture. **Please note: The material is hygroscopic.**

16. Methods of Analysis Requested

The following methods of analysis were requested:

- a) Multi element scan to include all elements by Multi-acid total digestion, including HF, ICP-OES or ICP-MS or AAS (particularly As, Cd, Hg, Pb)
- b) As, Cd, Hg, Pb by XRF pellet
- c) LOI and all majors oxides with XRF finish and/or Peroxide fusion and/or 4 acid digest including HF finished with either ICP-OES or ICP-MS or AAS (Please specify the temperature for LOI)
- d) Ca and Mg by HCl extraction and AAS finish
- e) SG – gas pycnometer
- f) S and C Combustion/LECO
- g) Moisture
- h) Activity

17. Information Requested of Participating Laboratories

The following information was requested of the participating laboratories for the development of this CRM:

- a) State aliquots used for all determinations.
- b) All results for major elements to be reported as oxides in percentages.
- c) All results for multi-element scans and fusion to be reported in ppm.
- d) Report all QC data, to include replicates, blanks and certified reference materials used.
- e) All Round robin samples must be treated the same as routine test samples.
- f) All results must be reported to maximum decimal places i.e. dependent on laboratories capabilities
- g) Please ensure moisture content is determined and calculated. All results should be corrected by the moisture correction factor and this factor should be stated in the laboratory results.
- h) Please use the excel template provided by AMIS. If you require a copy, please email any of the email addresses below. Ensure all uncertainties are added to the results.
- i) **Please send excel and PDF of all results.**
- j) Ensure correct PPE is used i.e. gloves, dust masks and protective clothing.
- k) Analysis should be done under controlled environmental conditions.

18. Certification of Mean and Estimation of Measurement Uncertainty

The samples used in this certification process have been selected in such a way as to represent the entire batch of material and were taken from the final packaged units; therefore, all sources of uncertainty are included in the combined standard uncertainty determination. Initially the data submitted by all the laboratories are subjected to a z-score test, equation [1] to exclude outliers and the remaining data sets examined for their normality in distribution. This is followed by the exclusion of further outliers as defined by the IUPAC Harmonised Protocol of 1995 in which both Cochran and a Grubbs test are applied until all outliers are identified, equations [2] and [3]. A grand mean and standard deviation is re-calculated using all remaining data (Thompson, 2008; Carr, 2011) (see Appendix 2)

19. Two Standard Deviations

AMIS reports two-standard deviations (2s) with all certified values. Two -standard deviations are calculated using the expression:

$$\text{Two standard deviations} = 2 (u_c)$$

Where u_c is the standard combined uncertainty (see Appendix, equation [14]).

20. Confidence Interval

AMIS reports a confidence interval (*CI*) with all certified values. Confidence interval as used by AMIS is:

$$\text{Confidence Interval (CI)} = \frac{(t_{\text{critical}})s}{\sqrt{N}}$$

Where, *N* is the number of laboratories (accepted laboratory data), t_{critical} is a two-tailed value for *N* – 1 degrees of freedom (*df*) and *s*, is the standard deviation of the accepted laboratory means. A two-tailed critical value is found for *N* -1 degrees of freedom from either a *t*-distribution table (Appendix 9) or MS Excel as =TINV (5%, *df*).

21. Expanded Uncertainty

ANOVA gives an estimate of the repeatability and the reproducibility of the data accepted for certification of the candidate reference material (see equations, [15] and [16], in the Appendix). Therefore, random variables (e.g., subsampling, instrument effects, interferences, operators and measurement conditions) that occur during the analysis of the candidate reference material by the various laboratories is considered. This approach does not necessarily quantify each individual source of uncertainty; however, the combined effect of random uncertainties is assessed (Ramsey & Ellison, 2007). A combined standard uncertainty is calculated from equation [14], which when multiplied by the *t*-critical value for *N*-1 laboratories, gives an *expanded uncertainty* at a 95% level of confidence. The expanded uncertainty is a measure of the doubt around the certified value at a level of 95% confidence. The expanded uncertainty is used in the validation of accuracy (see equation [18]).

22. Confidence Interval and Expanded Uncertainty

A combined standard uncertainty will be greater than a combined *CI*. This is because ANOVA considers the within-lab repeatability (that is repeatability within each lab group) as well as the repeatability between each lab data set. This attends to random variables that contribute to the measurement of uncertainty, during the analysis of the test sample at the participating laboratories. The within-lab repeatability and the between lab repeatability is combined as the square root of the sum of squares of these two values giving a combined standard uncertainty, at a 68% confidence level. Multiplying the combined standard uncertainty by the *t*-critical value for *N*-1, gives the expanded uncertainty at 95% level of confidence. It is recommended that the procedure described in Appendix 6, “Using the CRM in Quality Control” be used, in setting the limits of the CRM. Table 7 below shows mean gold values obtained by fire assay lead collection, for nine different laboratories, the confidence interval, two-standard deviations and expanded uncertainty.

Table 7. Example of replicate assay data in which the *CI*, 2*s* and *U* are shown.

Lab No.	Mean Au (g/t)	<i>CI</i>	0.0088
1	0.268	2s	0.031
2	0.273	U	0.04
3	0.270		
4	0.288		
5	0.274		
6	0.256		
7	0.263		
8	0.258		
9	0.288		

23. Participating Laboratories

The laboratories that are accredited with ISO17025 and provided timeous results are:

1. ALS Geochemistry Arabia
2. Argetest Mineral Processing, R&D and Analysis Services
3. Bureau Veritas Minerals Ultra Trace Pty Ltd
4. CRB Analyse Service GmbH
5. Dorfner Anzaplan (Analysenzentrum undAnlagenplanungsgesellschaft mbH)
6. Intertek Perth
7. Samancor Western Chrome Mine
8. SGS Geosol Laboratories Ltda (Brazil)
9. SGS Vancouver (Canada)

24. Accepted Assay Data

Data from the 9 laboratories used for certification are set out in Table 8.

Table 8. Data used to calculate the certified values after removal of outliers.

XRF	4A_MICP	XRF	LOI	SG	XRF	XRF	XRF	XRF	4A_MICP	4A_MICP	4A_MICP
Mg	Mg	MgO	LOI	SG	Al ₂ O ₃	CaO	Fe ₂ O ₃	SiO ₂	Al	Ca	Cd
ppm	ppm	%	%	Dimensionless	%	%	%	%	ppm	ppm	ppm
517380	513000	86.23	8.47	3.51	0.28	1.50	0.22	2.92	1200.00	10200	0.040
517020	516000	86.17	8.34	3.61	0.28	1.48	0.22	2.96	1100.00	10800	0.040
518460	522000	86.41	8.34	3.59	0.29	1.48	0.23	2.88	1200.00	11300	0.040
518100	515000	86.35	8.42	3.61	0.26	1.47	0.23	2.88	1300.00	11000	0.030
517980	515000	86.33	8.46	3.52	0.26	1.50	0.23	2.85	1300.00	10500	0.030
518520	526000	86.42	8.45	3.48	0.26	1.49	0.22	2.88	1200.00	10700	0.040
517560	513000	86.26	8.61	3.51	0.27	1.48	0.23	2.84	1300.00	10600	0.040
517260	512000	86.21	8.58	3.52	0.26	1.50	0.27	2.88	1300.00	9900	0.040
517800	501358	86.30	8.38	2.93	0.24	1.54	0.27	3.12	1400.00	10400	0.060
522000	517525	87.00	8.47	2.88	0.25	1.54	0.27	3.06	1300.00	10100	0.060
520800	496576	86.80	8.46	2.89	0.24	1.54	0.27	3.09	1300.00	10300	0.050
520800	519441	86.80	8.40	2.91	0.21	1.55	0.27	3.05	1300.00	10000	0.050
520800	507277	86.80	8.46	2.92	0.23	1.54	0.27	3.12	1300.00	10100	0.060
522000	514654	87.00	8.41	2.92	0.24	1.53	0.26	3.08	1300.00	10800	0.050
519000	504971	86.50	8.50	2.90	0.22	1.55	0.27	3.09	1300.00	10800	0.060
523200	502041	87.20	8.40	2.93	0.20	1.54	0.27	3.10	1500.00	10600	0.040
513600		85.60	8.55		0.25	1.63	0.26	3.23	1300.00	10900	
512100		85.35	8.60		0.27	1.61	0.27	3.23	1400.00	10900	
511320		85.22	8.45		0.26	1.62	0.26	3.21	1500.00	10700	
512640		85.44	8.52		0.25	1.63	0.26	3.20	1300.00	10400	
514560		85.76	8.35		0.24	1.63	0.27	3.18	1400.00	11200	
514320		85.72	8.30		0.25	1.63	0.26	3.24	1300.00	10800	
513720		85.62	8.61		0.25	1.62	0.26	3.22	1400.00	10600	
513660		85.61	8.24		0.25	1.63	0.25	3.23	1300.00	10900	
505770		84.30	9.11		0.24	1.53	0.25	3.20		10500	
503526		83.92	8.90		0.24	1.53	0.24	3.20		10600	
503754		83.96	9.13		0.24	1.51	0.25	3.22		10700	
503172		83.86	9.35		0.22	1.53	0.25	3.18		10400	
508122		84.69	8.78		0.25	1.53	0.25	3.17		10400	
509004		84.83	8.65		0.21	1.52	0.25	3.21		10200	
503694		83.95	8.79		0.23	1.52	0.25	3.20		10600	
505908		84.32	8.78		0.23	1.53	0.28	3.22		10800	
512700		85.45	9.66		0.23	1.51	0.28	3.19		10500	
510840		85.14	9.01		0.23	1.51	0.28	3.20		10700	
512580		85.43	8.81		0.23	1.50	0.28	3.21		10700	
512220		85.37	8.86		0.28	1.49	0.28	3.25		11200	
512760		85.46	8.46		0.24	1.53	0.26	3.22		11000	
512340		85.39	8.67		0.25	1.50	0.28	3.16			
513240		85.54	8.96		0.24	1.51	0.27	3.24			
511980		85.33	9.38		0.25	1.49	0.31	3.17			
516840		86.14	8.63		0.24	1.41	0.31	3.16			
516300		86.05	8.70		0.24	1.41	0.31	3.15			
516360		86.06	8.67		0.24	1.39	0.31	3.16			
516660		86.11	8.56		0.24	1.40	0.31	3.16			
516360		86.06	8.68		0.24	1.40	0.27	3.15			
516360		86.06	8.71		0.24	1.41	0.27	3.19			
515880		85.98	8.62		0.24	1.57	0.27	3.12			
516840		86.14	8.81			1.56	0.28	3.16			
						1.55	0.29				
						1.56	0.28				
						1.55	0.28				
						1.57	0.27				
						1.56					
						1.55					

Assay Data (Cont.)

4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP	4A_MICP
Ce	Cu	La	Mo	Na	Ni	Pb	Rb	Sb	Sr	U	W	Zn
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
0.91	15.90	0.40	0.16	1400	8.00	13.00	1.50	0.73	171.00	0.32	0.50	14.00
1.00	16.00	0.50	0.15	1400	10.00	11.00	1.50	0.76	178.50	0.33	0.50	13.00
0.94	17.10	0.50	0.15	1400	8.00	13.00	1.50	0.81	172.60	0.33	0.50	14.00
0.89	17.50	0.40	0.15	1400	10.00	13.00	1.40	0.83	175.70	0.30	0.50	13.00
0.97	15.90	0.50	0.14	1400	8.00	12.00	1.40	0.82	175.80	0.33	0.50	13.00
0.97	17.70	0.50	0.15	1400	9.00	13.00	1.60	0.86	180.60	0.32	0.50	14.00
0.94	16.90	0.50	0.14	1400	8.00	14.00	1.60	0.87	177.90	0.33	0.50	13.00
0.83	15.70	0.40	0.14	1400	6.00	15.00	1.50	0.88	173.70	0.33	0.50	14.00
1.30	15.00	0.70	0.10	1400	6.40	13.70	1.60	0.60	185.00	0.30	0.40	12.00
1.40	15.00	0.80	0.10	1500	6.60	14.90	1.60	1.00	175.00	0.30	0.40	13.00
1.30	14.00	0.70	0.20	1400	6.70	14.70	1.40	0.60	182.00	0.30	0.30	13.00
1.30	15.00	0.70	0.10	1400	6.60	14.30	1.40	0.60	176.00	0.30	0.50	11.00
1.30	16.00	0.70	0.20	1400	6.20	14.20	1.40	0.80	183.00	0.30	0.40	11.00
1.30	15.00	0.70	0.20	1500	6.90	15.00	1.40	0.80	183.00	0.30	0.50	11.00
1.30	15.00	0.70	0.10	1400	6.60	13.60	1.40	1.20	178.00	0.30	0.30	11.00
1.30	14.00	0.80	0.20	1400	6.40	16.00	1.40	0.80	180.00	0.30	0.50	11.00
	10.50	0.74	0.40	1400	7.00	16.00	1.20	0.80	209.00	0.33		10.00
	10.40	0.68	0.25	1400	8.00	17.00	1.40	0.90	211.00	0.33		11.00
	10.80	0.64	0.22	1400	7.00	17.00	1.20	0.80	200.00	0.35		12.00
	11.00	0.53	0.19	1400	7.00	16.00	1.30	1.00	202.00	0.31		11.00
	11.50	0.53	0.20	1400	8.00	12.00	1.40	0.90	210.00	0.33		11.00
	10.30	0.55	0.19	1400	8.00	13.00	1.20	1.00	206.00	0.32		12.00
	13.00	0.69	0.20	1300	7.00	15.00	1.40	1.00	209.00	0.36		11.00
	14.00	0.67		1300	8.00	13.00	1.66	0.80	209.00			12.00
	14.00			1500	8.22	14.00	1.67	0.72	199.00			13.07
	13.00			1500	7.65	14.00	1.70	0.49	207.00			17.37
	15.00			1500	7.57	12.00	1.70	0.88	204.00			16.62
	14.00			1500	7.55	14.00	1.60	0.50	200.00			15.26
	14.00			1500	7.77	14.65	1.65	0.61	205.00			15.07
	15.00			1500	7.43	16.01	1.67	0.43	209.00			11.94
	16.12			1600	8.29	14.07		0.67	205.00			15.44
	16.25			1600	8.32	13.87			200.00			13.70
	17.38					14.18			183.28			
	16.99					14.10			190.64			
	16.32					14.62			193.45			
	15.54					15.67			189.00			
	17.71								191.21			
	18.41								192.84			
									202.20			
									197.58			

25. Reported Values

The certified values listed in this certificate fulfil the AMIS statistical criteria (see section 18) regarding agreement for certification and have been independently validated by Allan Fraser.

26. Validation of Accuracy (Trueness)

This CRM can be used to validate accuracy (trueness) as required in method validation as stated in the ISO17025 standard. See Appendix 3 for an example on the validation of accuracy using replicate data derived from the analysis of a CRM.

27. Metrological Traceability

The values quoted herein are based on the consensus values derived from statistical analysis of the data from an inter-laboratory measurement program. Traceability to SI units is via the standards used by the individual laboratories the majority of which are accredited to the ISO17025 general requirements for the competence of testing and calibration laboratories and who have maintained measurement traceability during the analytical process.

28. Period of Validity

The certified values are valid for this product, while still sealed in its original packaging, until notification to the contrary. The stability of the material will be subject to continuous testing for the duration of the inventory. Should product stability become an issue, all customers will be notified and notification to that effect will be placed on the www.amis.co.za website.

29. Minimum Sample Size

The majority of laboratories reporting used a 0.5g sample size for the ICP-OES and a 30g sample size for the fire assay. These are the recommended minimum sample sizes for the use of this material.

30. Availability

This product is available in Laboratory Packs containing 1kg of material and Explorer Packs containing custom weights (from 50 to 250g) of material. The Laboratory Packs are sealed bottles delivered in sealed foil pouches. The Explorer Packs contain material in standard geochem envelopes, nitrogen flushed, and vacuum sealed in foil pouches.

31. Recommended use in Quality Control

Users should set their own limits *i.e.* 1, 2 and 3 standard deviations from an obtained mean value based on at least 10 replicate analyses using this CRM (see Appendix 6 for detail on the use of this CRM in quality control).

32. Legal Notice

This certificate and the reference material described in it have been prepared with due care and attention. However, AMIS, Melesha Mungaroo and Allan Fraser; accept no liability for any decisions or actions taken following the use of the reference material.

Date of Version 000: 12 November 2019

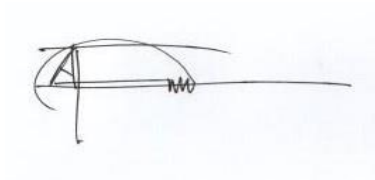
Version: 000

Approving Officer:

African Mineral Standards: _____

Melesha Mungaroo (Technical Manager)

Certifying Officer:

A handwritten signature in black ink, appearing to be 'A. Fraser', written over a horizontal line.

Geochemist: _____

Allan Fraser

M.Sc. (Geology), N.D. (Analytical Chem.),
Pr.Sci.Nat. Pr.Chem.SA

References

- Abzalov, M. (2011). Sampling Errors and Control of Assay Data Quality in Exploration and Mining Geology, Applications and Experiences of Quality Control. Ivanov, O., (Ed.), InTech, DOI: 10.5772/14965. Available from: <http://www.intechopen.com/books/applications-and-experiences-of-quality-control/sampling-errors-and-control-of-assay-data-quality-in-exploration-and-mining-geology>. Accessed 25th September, 2016.
- ASTM E122-09e1, Standard Practice for Calculating Sample Size to Estimate, With Specified Precision, the Average for a Characteristic of a Lot or Process, ASTM International, West Conshohocken, PA, 2011, www.astm.org
- Barwick V.J., Pritchard E. (Eds). (2011). Eurachem Guide; Terminology in Analytical Measurement – Introduction to VIM 3 (2011). ISBN 978-0-948926-29-7.
- Carr R.H. (2011). Estimating errors using graphs and taking good data. California State University Los Angeles. March 2011. 14. <http://web.calstatela.edu/faculty/kaniol/Err-Gph-Meas-IBooklet.pdf>. Retrieved: 29 August, 2016.
- Cochran, W.G. (1950). The Comparison of Percentages in Matched Samples. *Biometrika*, 37, 256-66.
- Ellison, S., Barwick, V., Duguid Farrant, T. (2009). *Practical statistics for the analytical scientist, a bench guide. 2nd Edition*. RSC Publishing. 25-172.
- ERM Application Note 1. (2005). Comparison of a measurement value with a certified value. European Commission – Joint Research Centre Institute for Reference Materials and Measurements (IRMM). 1-2.
- EURACHEM / CITAC Guide CG 4. (2012). Quantifying uncertainty in analytical measurement. 3rd Edition. Editors: Ellison, S. L. R., Williams, A. 4-121.
- Eurolab Technical Report No.1/2007. (2007). Measurement uncertainty revisited: Alternative approaches to uncertainty evaluation. European Federation of National Associations of Measurement, Testing and Laboratories. 43-46.
- Fraser, A.W. (2015). Minimising uncertainty in measurement and improving limit of detection in gold bearing ores from concentrations predicted by linear regression in atomic absorption spectrometry. M.Sc. thesis (unpublished), University of Johannesburg: 199 pages.
- Grubbs, F.E. (1969). Procedures for detecting outlying observations in samples. *Technometrics*, 11, 1969. 1-21.
- Horwitz, W., Albert, R. (2006). The Horwitz Ratio (HorRat): A useful index of method performance with respect to precision, *Journal of Association of Official Analytical Chemists International*, 89: 1095-1109.
- ISO/IEC 17025:2005(E). (2005). *General requirements for the competence of testing and calibration laboratories*. 2nd Edition: 14-59.
- ISO Guide 35 (2003). Certification of reference materials — General and Statistical principles, 3rd edition. ISO/REMCO WG 1.
- ISO 5725-2:1994. Accuracy (trueness and precision) of measurement methods and results -- Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.
- Long, J., Winefordner, J. (1983). Limit of detection - a closer look at the IUPAC definition. *Analytical Chemistry* 55: 712A - 724A.
- Miller, J., Miller, J. (2010). *Statistics for analytical chemistry*. 6th Edition. New York: Ellis Horwood. 36-126.
- Nelsen T.C., Wehling P. (2008). Collaborative studies for quantitative chemical analytical methods. AACC International Report. *Cereal Foods World*. September – October 2008, Vol. 53, No. 5. 285-288.
- Skoog, D., West, D. (1982). *Fundamentals of analytical chemistry*. 4th Edition. CBS College Publishing. Holt Saunders International Editions: 39-73.
- Thompson, M. (Ed.) (2008). Test for 'sufficient homogeneity' in a reference material. Analytical Methods Committee, AMCTB 17A, ISSN 1757-5958.
- Thompson, M. (Ed.) (2010). Internal quality control in routine analysis. AMC Technical Brief. Analytical Methods Committee. AMCTB No.46. 2010. Issn 1757-5958.
- Thompson, M., Lowthian, P. (2011). *Notes on statistics and data quality for analytical chemists*. Imperial College Press: 15-115.

Appendices

Appendix 1: Uncertified Element Statistics

Uncertified element statistics are shown in **Table 9**.

Table 9. Uncertified element concentrations statistics.

Element	Generic Method	n	Mean	SD	RSD %	Unit
Ag	4A_MICP	15	0.1	0.01	25	ppm
Ba	4A_MICP	40	19.3	6.3	32	ppm
Ba	FUS ¹⁰	7	39.9	3.2	8	ppm
BaO	XRF	6	0.01	*	*	%
Be	4A_MICP	17	0.1	0.04	28	ppm
Bi	4A_MICP	32	1.4	2.4 #	173	ppm
C	Combustion/LECO ¹¹	40	13825	1907	14	ppm
Ca	4A_AAS ¹²	8	10797	294	3	ppm
Co	4A_MICP	33	1.8	1.0	55	ppm
Cr	4A_MICP	48	46.3	15.6	34	ppm
Cr	FUS	6	172.8	6.1	4	ppm
Cr ₂ O ₃	XRF	48	0.03	0.01	31	%
Cs	4A_MICP	3	0.1	*	*	ppm
Dy	4A_MICP	8	0.1	0.02	19	ppm
Er	4A_MICP	4	0.1	*	*	ppm
Fe	4A_MICP	40	1655	327	20	ppm
Fe	FUS	8	1993	85	4	ppm
Ga	4A_MICP	32	0.3	0.2	46	ppm
Hf	4A_MICP	10	0.2	0.1	64	ppm
K	4A_MICP	40	340	51	15	ppm
K	FUS	8	1154	148	13	ppm
K ₂ O	XRF	48	0.04	0.005	13	%
Li	4A_MICP	40	19.8	6.1	31	ppm
LOI	LOI gravimetric ¹³	8	12.3	1.0	8	%
LOI	LOI TGA ¹⁴	8	12.7	1.1	9	%
LOI	LOI XRF ¹⁵	8	12.9	1.1	8	%
Lu	4A_MICP	4	0.01	0.01	40	ppm
Mg	4A_AAS	8	509538	3655	1	ppm
MgO	Ext ¹⁶	8	83.6	0.2	0.2	%
MgO	FUS	8	83.9	0.4	1	%
Mn	4A_MICP	32	21.1	4.0	19	ppm
Mn	FUS	8	30.1	2.0	7	ppm

Element	Generic Method	n	Mean	SD	RSD %	Unit
MnO	XRF	10	0.006	0.002	37	%
Moisture	Moisture ¹⁷	22	1.600	0.1	6	%
Na	4A_AAS	8	1288	35	3	ppm
Na ₂ O	XRF	56	0.2	0.1	49	ppm
Nb	4A_MICP	23	1.2	1.2 #	98	ppm
Nd	4A_MICP	8	0.6	0.03	4	ppm
P	4A_MICP	16	46.9	4.8	10	ppm
P ₂ O ₅	XRF	28	0.01	0.002	22	%
Pr	4A_MICP	8	0.2	0.000000002	0.000001	ppm
S	4A_MICP	48	0.02	0.005	30	%
S	Combustion/LECO	29	0.02	0.01	41	%
Sc	4A_MICP	8	0.9	0.2	25	ppm
Sm	4A_MICP	8	0.1	0.03	20	ppm
Sn	4A_MICP	8	0.4	0.3	67	ppm
SO ₃	XRF	16	0.04	0.01	19	%
Sr	FUS	8	208.5	3.0	1	ppm
SrO	XRF	16	0.02	0.001	7	%
Ta	4A_MICP	22	1.4	2.0 #	142	ppm
Te	4A_MICP	15	0.2	0.1	63	ppm
Th	4A_MICP	20	0.4	0.7 #	192	ppm
Ti	4A_MICP	24	86.0	35.7	41	ppm
Ti	FUS	8	102.4	2.6	3	ppm
TiO ₂	XRF	45	0.02	0.004	26	%
Tl	4A_MICP	1	0.1	*	*	ppm
V	4A_MICP	40	6.8	1.9	28	ppm
V	FUS	8	16.8	1.4	8	ppm
V ₂ O ₅	XRF	1	0.01	*	*	%
Y	4A_MICP	32	0.4	0.1	40	ppm
Yb	4A_MICP	8	0.1	0.02	17	ppm
Zr	4A_MICP	32	4.2	1.7	41	ppm
Zr	FUS	6	25.2	1.8	7	ppm

* denotes that the results were exactly the same and SD and RSD% could not be calculated
denotes that the SD>Mean

Appendix 2 through 9, prepared by Allan Fraser.

Appendix 2. Certification of Reference Material and Estimation of Measurement Uncertainty

In the establishment of a consensus value for the CRM, outlier tests are carried out followed by performance statistics and the estimation of the measurement uncertainty. In practice, it is highly likely that data generated by multiple laboratories as an inter-laboratory comparison of material for certification, will contain erroneous as well as extreme measurements (outliers). The influence of outliers on summary statistics needs to be minimised by the application of procedures for outlier identification on raw data. The use of z-scoring, Cochran's test for suspect repeatability variances, along with Grubbs test for suspect measurement values allows for the detection of outliers (IUPAC, 1995). Method performance in terms of precision as relative standard deviation is judged by the application of the Horwitz ratio, which gives an indication of whether the observed relative standard deviation at the concentration levels of analyte determined are acceptable (Horwitz & Albert, 2006).

In the absence of an extensive uncertainty budget, measurement uncertainty is estimated from the reproducibility standard deviation from inter-laboratory data and reported as an expanded uncertainty at a level of confidence of 95% (Miller & Miller, 2010).

The steps below give detail on the establishment of a consensus value through the elimination of outliers, method performance and estimation of measurement uncertainty using standard uncertainties and the analysis of variance.

Z-Score

A z-score is calculated using equation [1]:

$$z = \frac{x - x_a}{s_p} \quad [1]$$

Where, x is the result of a submitted sample, x_a is the mean and s_p is the standard deviation of the submitted results from all the participating laboratories. Z-Scores are interpreted as follows:

$|z| \leq 2$ satisfactory performance
 $2 < |z| \leq 3$ questionable performance
 $|z| > 3$ unsatisfactory performance

(Thompson & Lowthian, 2011)

Data with z-scores exceeding two are discarded and are not included for further assessment.

Cochran's Test

The test of Cochran (1950) as shown in equation [2] is applied to any suspect repeatability variances:

$$C_{calc} = \frac{s_{max}^2}{\sum_{i=1}^l s_i^2} \quad [2]$$

Where, C_{calc} , s_{max}^2 and $\sum_{i=1}^l s_i^2$, are the calculated values for Cochran's test, data set with the maximum variance and the sum of the variances of all of the participating, l laboratory datasets. The C_{calc} value is compared with a critical value, C_{crit} at a level of confidence of 95% and an alpha of 0.05% (see Ellison, *et al.*, 2009, Appendix A, Table A.3a, page 209 for a table of critical values for the test of Cochran at LOC 95%).

According to ISO 5725-2 (1999), results from a laboratory with a suspect repeatability variance can be excluded if it is shown by the Cochran test to be an outlier. Therefore, if $C_{calc} > C_{crit}$, the laboratory with the maximum variance is removed. The data found to be excluded should not be $>2/9$, or 22% of the total data.

Grubbs Test

The test of Grubbs (1969) calculates a test statistic, G_{calc} and in the detection of a single outlier, G_1 is found by using

$$G_{1\,calc} = \frac{|Suspect\ value - \bar{x}|}{s} \quad [3]$$

Where, the sample mean and standard deviation, \bar{x} and s , are calculated with the suspect value included. The $G_{1\,calc}$ statistic is compared to a critical value for N measurements. See Ellison, *et al.*, 2009, Appendix A, Table A.2, page 208 for a table of critical values for the test of Cochran at LOC 95%.

Method Performance

The Horwitz function is used to assess the performance of the data under consideration, with respect to precision (Horwitz & Albert, 2006). A calculated %RSD is found using the Horwitz expression

$$\%RSD = \pm 2^{(1-0.5\log C)} \quad [4]$$

where, C is the analyte concentration in percent divided by 100 and \log is the natural logarithm. The observed %RSD is calculated as

$$Observed\ \%RSD = \frac{s}{Mean} \times 100 \quad [5]$$

where s is the standard deviation of n replicates.

The ratio of the observed %RSD and the calculated %RSD gives the Horwitz ratio (HorRat):

$$HorRat = \frac{\%RSD\ Observed}{\%RSD\ Calculated} \quad [6]$$

A HorRat <2 indicates that the method is of adequate precision. Should the HorRat be >2 the overall data are discarded, and the candidate material considered not suitable for certification as the precision is excessive for the concentration of the analyte being determined (Nelsen & Wehling, 2008).

Grand Mean

The grand mean ($\bar{\bar{x}}$) *i.e.* the certified value of a dataset is the total of all the data values divided by the total sample size (n):

$$\bar{\bar{x}} = \sum \frac{x}{n} \quad [7]$$

Certified Value

From ANOVA as per the description in section 18, an 'appropriate precision' as shown in [8] is calculated for sufficient homogeneity (Thompson, 2008):

$$s_r \leq 0.3u_c \quad [8]$$

Where, s_r is the within laboratory repeatability, as determined from [14]. Once [8] is satisfied, a grand mean [7] is calculated and this is taken to be the certified value.

Total Variation (SST)

The total variation (not the variance) comprises the sum of the squares of the differences of each mean with the grand mean.

$$SST = \sum (x - \bar{x})^2 \quad [9]$$

Between Group Variation (SSB)

The *variation* due to the between the laboratories is denoted SSB or Sum of Squares Between laboratories and given by [10]. If the laboratory means are close to each other (and therefore the Grand Mean) SSB will be a small value. There are P samples involved with one datum value for each sample (the sample mean), so there are P-1 degrees of freedom.

$$SSB = \sum n(\bar{x} - \bar{\bar{x}})^2 \quad [10]$$

The *variance* due to the interaction between the laboratories is denoted MSB for Mean Square Between groups and is the SSB divided by its degrees of freedom.

$$MS = \frac{SSB}{n - 1} \quad [11]$$

Within Group Variation (SSW)

The variation due to differences within individual samples is denoted SSW for Sum of Squares Within laboratories. The degrees of freedom are equal to the sum of the individual degrees of freedom for each sample. Since each sample has degrees of freedom (*df*) equal to one less than their sample sizes, and there are k samples, the total degrees of freedom is P less than the total sample size: $df = n - P$.

$$SSW = \sum df \cdot s^2 \quad [12]$$

The variance due to the differences within individual samples is denoted MSW for Mean Square Within groups. This is the within group variation divided by its degrees of freedom:

$$MSW = \frac{SSW}{P - n} \quad [13]$$

From equations [9] through [13], the ANOVA table as shown in Table 10 is developed.

Table 10. A single-factor ANOVA table showing key elements. Where P is the total number of groups, or laboratories. P-1 is 1 less than number of laboratories, P (n-1) is the number of data values minus number of groups (equals degrees of freedom for each group added together), and P-1 + P(n-1) is 1 less than the number of data points. MS is the mean squares of between laboratories and within laboratories. After Ellison *et al.*, (2009), Table 6.2, page 61.

Source	Sum of Squares	df	Mean Sum of Squares	F	p	F _{crit}
Between Laboratories	SSB	P-1	MSB=SSB/df	MSB/MSW	=FDIST(x,df,df)	F-table
Within Laboratories	SSW	P(n-1)	MSW=SSW/df	–	–	–
Total	SSB+SSW	P-1 + P(n-1)	–	–	–	–

Combined Standard Uncertainty

The combined standard uncertainty (u_c) represents the effects of random events such as days, instruments, and analysts on the precision of the analytical procedures of all accepted data of the participating laboratories. Using the output from ANOVA, the combined standard uncertainty (u_c) is determined from the square root of the sum of squares of the variances of the within laboratory repeatability, s_r , and the between laboratory precision, s_s :

$$u_c = \sqrt{s_r^2 + s_s^2} \quad [14]$$

Within laboratory repeatability is determined as

$$s_r = \sqrt{MSB} \quad [15]$$

and, the between laboratory precision as

$$s_s = \sqrt{\frac{(MSW - MSB)}{n}} \quad [16]$$

where MSW is the mean squares of the within laboratory variance, MSB is the mean squares for the between laboratories and n in this case, is the number of replicates in a group of the accepted data (Thompson & Lowthian, 2011).

Expanded Uncertainty

The expanded uncertainty (U) at a confidence level of 95% is determined by multiplication of the combined uncertainty (u_c) by a coverage factor (k) found from $N-1$ degrees of freedom (df), where N is the number of laboratory means accepted in the establishment of the certified value. The t-critical value for 5% significance can be found in a t-critical table (see Appendix 9, or from MS Excel as =TINV (5%, df)).

Uncertainty Statement

Typically, an uncertainty statement is presented as follows: Au =0.77±0.04 g/t, where the number following the symbol ± is the numerical value of an expanded uncertainty, $U = ku_c$, with U determined from a combined standard uncertainty multiplied by a coverage factor $k = 2$ or, a t-critical value for $N-1$ accepted laboratories. Since it can be assumed that the possible estimated values of the standard are approximately normally distributed with standard uncertainty, u_c , the certified value of the CRM is believed to lie in the interval defined by U with a level of confidence of approximately 95 %, e.g. a mean value of 0.77±0.04g/t will have intervals of: 0.73≤0.77≤0.81 g/t.

Appendix 3. Example: Comparison of Mean and Certified Value for Validation of Accuracy

According to ERM (2005); Eurolab (2007); Abzalov (2011) and Carr (2011), the validation of accuracy for a given mean and certified value requires the inclusion of the measurement uncertainty of the CRM in a t-test for statistical significance. The classical Student's t-test as shown in [17], does not consider the measurement uncertainty of the CRM. To compensate for this, Eurolab Technical Report No.1/2007 recommends equation [18] for the validation of CRMs with stated measurement uncertainties.

$$t_{calc} = \frac{|\bar{x} - \mu|}{\frac{s}{\sqrt{n}}} \quad [17]$$

$$t_{calc} = \frac{|\bar{x} - \mu|}{\sqrt{(u_{\mu})^2 + \frac{s^2}{n}}} \quad [18]$$

Where, t_{calc} is the calculated t-statistic, \bar{x} the mean of n replicates with a standard deviation of s for a CRM of μ certified value. The standard uncertainty u is the stated expanded uncertainty (U) of the CRM divided by the coverage factor (k) as stated on the certificate of analysis. Note that the $| \quad |$ bars indicate that the absolute value between the mean and the certified value is to be used, *i.e.* ignore the sign.

An example in which [18] is used for validation of accuracy is given below.

Example

A CRM is independently replicated nine times for Al_2O_3 concentration by XRF analysis, *i.e.* 9 individual fused glass beads were prepared. The observed mean and standard deviation of the replicate data are shown with the certified value and expanded uncertainty in Table 11. In validation of accuracy, the hypothesis question is: Is the difference between the observed mean and the certified value statistically significant at a level of confidence of 95%? Alternatively put, is there sufficient evidence to conclude that the data *i.e.* replicates generated, are inaccurate?

The relevant hypotheses are:

Null hypothesis: H_0 : Mean = Certified value of CRM with stated measurement uncertainty. The acceptance of H_0 means that accuracy is demonstrated; *i.e.* insufficient evidence to reject H_0 ;

Alternate hypothesis: H_1 : Mean \neq Certified value of CRM with stated measurement uncertainty. The acceptance of H_1 means that accuracy is not demonstrated, *i.e.* there is sufficient evidence to accept H_1 ;

Table 11. CRM certified value, quoted expanded uncertainty U , the coverage factor for the CRM, $k=2.25$ and mean for $n=9$ replicates and corresponding standard deviation for the replicate data.

CRM Certified Value	Expanded % (U)	Coverage Factor (k)	Mean ($n=9$)	n	Standard Deviation (s)
4.62%	0.08%	2.25	4.59%	9	0.01015

The standard uncertainty (u) is found by dividing the expanded uncertainty by the coverage factor:

$$u = \frac{0.08}{2.25} = 0.0356 \%$$

Using the observed mean for the replicate data ($n=9$) obtained for the CRM and substituting into [18]:

$$t_{calc} = \frac{|\bar{x} - \mu|}{\sqrt{0.0356^2 + \frac{0.01015^2}{9}}} = \frac{|4.59 - 4.62|}{\sqrt{0.00126 + 0.00001145}} = 0.84$$

Therefore, $t_{calc} = 0.84$ and $t_{crit}(5\%, 8) = 2.31$ (df is 8, therefore, $t_{crit}=2.31$, see Appendix 9, page 29) which is >0.84 . Similarly, the p -value=0.43 which is >0.05 . This is strong evidence in favour of accepting the null hypothesis that there is no significant statistical difference between the certified value and the observed mean. Therefore, under the conditions that the uncertainty associated with the certified value is known, the accuracy is validated for the CRM tested. If the null hypothesis is accepted that the mean obtained is not statistically different from the certified value, then the principle of traceability has been conformed to.

Appendix 4. Two-standard Deviations

Two-standard deviations are calculated using the expression:

$$\text{Two standard deviations} = 2 (u_c) \quad [19]$$

Where, u_c is the standard combined uncertainty (equation [14]).

Appendix 5. Confidence Interval

Confidence interval is calculated as:

$$\text{Confidence Interval (CI)} = \frac{(t_{critical})s}{\sqrt{N}} \quad [20]$$

Where, N is the number of laboratories (accepted laboratory data), $t_{critical}$ is a two-tailed value for $N - 1$ degrees of freedom (df) and s , is the standard deviation of the accepted laboratory means. A two-tailed critical value is found for $N - 1$ degrees of freedom from either a t -distribution table (Appendix 9) or MS Excel as =TINV (5%, df).

Appendix 6. Using the CRM in Quality Control

QC chart control limits should not be determined by the certified value and stated measurement uncertainty of the certified reference material used. These parameters although “certified” will never be known; it is only the corresponding statistical estimates, *i.e.* standard deviation and the mean calculated from replicated results that are known and these should be used in quality control charts. However, should the laboratory choose to use the certified value as the mean then the quoted $2s$, or CI value for the CRM can be used in the quality control chart.

It is recommended that a Shewhart chart be developed for the use if this CRM is to be used as a control sample in laboratory quality control. A Shewhart chart is a plot of sequential assay results obtained from quality control material such as an AMIS CRM. The warning and control limits are based on the standard deviation obtained from the mean of the replicates of a CRM (Ellison, *et al.*, 2009; Thompson, 2010). The procedure in preparing a Shewhart chart is as follows:

1. Analyse 10 to 15 replicates or more of the AMIS CRM.
2. Apply the Grubbs test for outliers.
3. Determine the mean of the replicates after application of the Grubbs test.
4. Determine the standard deviation, using equation [21], of the replicates following Grubbs test.
5. Calculate the standard deviation, s from:

$$s = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n - 1}} \quad [21]$$

where, x_i is an individual measurement in the data set, \bar{x} is the mean of the data set at $n-1$ degrees of freedom (df) and n is the number of replicates. The sample standard deviation can be found using the MS Excel formula “=stdev.s (number1;)”.

6. Verify accuracy of the mean value using equation [18].
7. Once accuracy is verified, calculate $\pm 2s$ and $\pm 3s$, where s is the standard deviation calculated from [21].
8. Construct the Shewhart control chart around the mean of n replicates.
9. Use $\pm 2s$ as the warning limits.
10. Use $\pm 3s$ as the control limits.
11. It is recommended that if 2 to 3 points are outside the warning limits analyse another sample and if it is then within warning limits, continue. If it is outside the warning limits, stop and troubleshoot.
12. It is recommended that if any point is outside control limits, analyse another portion (sample) of the CRM. If it is within control limits, continue. If it is outside control limits, stop and troubleshoot.
13. For reference purposes, the CRM certified value can be plotted on the Shewhart chart alongside the mean value.

On a regular basis the accuracy of the replicates of the CRM should be assessed in terms of the certified value of the CRM using equation [18].

Appendix 7. Conversion to Air-dry Basis (Prepared by Allan Fraser)

Since AMIS certified analyte values are reported on a dry-basis, the user laboratory is required to dry a portion (accurately weigh out 1.0 grams in duplicate) of the CRM material in air at 105°C in a drying oven to constant mass to determine the moisture content. Use a crucible with a flat inner surface with a surface area not smaller than 10 cm² with the CRM material spread evenly over same; this represents a 0.1 gram spread per cm². In correcting the certified value for moisture content, a moisture correction factor is calculated:

$$\text{Moisture correction factor (MCF)} = \frac{100 - \% \text{Moisture at } 105^{\circ}C}{100} \quad [22]$$

$$\text{Air dry basis concentration} = \text{MCF} \times \text{certified value on a dry basis} \quad [23]$$

Example

The moisture content determined at 105°C on a CRM is 0.500%. The certified analyte concentration for the CRM is 12.62±0.52% (dry basis). Calculating the moisture correction factor using [22] gives:

$$\text{Moisture correction factor} = \frac{100 - 0.500}{100} = 0.995$$

Multiplying the factor of 0.995 by the certified value as stated on the certificate of analysis on a dry basis (as in [23]) gives the analyte concentration on an air-dry basis:

$$0.995 \times 12.62\% = 12.56\%$$

The stated measurement uncertainty also needs to be corrected using [22] and [23], e.g. $0.995 \times 0.52 = 0.51_{(7)}$, rounded to 0.52%. The air-dry basis concentration *i.e.* $12.56 \pm 0.52\%$ is to be used as the certified value with its corresponding measurement of uncertainty.

Appendix 8. Example of Determination of LOD and LOQ in Fire Assay

The limit of detection (LOD) is the minimum detectable quantity of the analyte of interest (Skoog & West, 1985). To determine the LOD in fire assay by lead collection, the minimum mass that an assay microbalance is capable of weighing (m in micrograms, and the original test sample mass, $Mass_{assay}$ in grams) determines the LOD. The smallest prill mass most assay microbalances can measure is $1\mu\text{g}$ or 0.001mg . Even with a microscope it may be difficult to locate and pick up a prill weighing ten times that amount (*i.e.* 0.01mg or $10\mu\text{g}$) and weigh it. If an analyst can weigh a prill of $1\mu\text{g}$ then the LOD becomes $1\mu\text{g}$. However, the concentration factor would be 50 times for a 50-gram assay sample and therefore the LOD in g/t becomes $1\mu\text{g}$ divided by the original mass of the sample in grams taken for fire assay [24]. Therefore, the LOD in fire assay is computed as:

$$LOD = \frac{m (\mu\text{g})}{Mass_{assay} (g)} (\text{g/t}) \quad [24]$$

The limit of quantitation (LOQ), is simply the LOD multiplied by 10 (Long & Winefordner, 1983):

$$LOQ = 10 \cdot \frac{m (\mu\text{g})}{Mass_{assay} (g)} (\text{g/t}) \quad [25]$$

Therefore, with a sample mass of 50g taken for fire assay, the limit of detection would be 0.02g/t . *i.e.* $1\mu\text{g} = 1\text{g/t}$, therefore $1\mu\text{g}/50\text{g} = 0.02\text{g/t}$. If no prill was found, then the LOD result would be $<0.02\text{g/t}$ or "not detected". Using a larger assay sample mass improves the LOD and LOQ (Table 11). Table 13 gives a recommended reporting scheme for LOD and LOQ.

Table 12. Mass of assay sample and corresponding limit of detection and limit of quantitation for an assay microbalance capability of smallest prill mass of $1\mu\text{g}$ or 0.001mg .

Mass Assay Sample (g)	LOD (g/t)	LOQ (g/t)
30	0.03	0.3
50	0.02	0.2
100	0.01	0.1

Table 13. Recommended reporting scheme for LOD and LOQ in fire assay.

Data	Report as
<LOD	Not detected
<LOQ	Detected
$\geq\text{LOQ}$	Report assay result

Appendix 9. T-distribution table

Table 14. T-distribution table for t-critical values (t crit.) for a two-tailed t-test at a 95% level of confidence.

df	Two-tailed	df	Two-tailed
1	12.71	23	2.06
2	4.30	24	2.06
3	3.18	25	2.06
4	2.78	26	2.05
5	2.57	27	2.05
6	2.44	28	2.04
7	2.36	29	2.04
8	2.30	30	2.04
9	2.26	35	2.03
10	2.22	40	2.02
11	2.20	45	2.01
12	2.17	50	2.00
13	2.16	55	2.00
14	2.14	60	2.00
15	2.13	70	1.99
16	2.12	80	1.98
17	2.11	90	1.98
18	2.10	100	1.98
19	2.09	120	1.98
20	2.08	Infinity	1.96
21	2.08		
22	2.07		

End of certificate